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16. ABSTRACT

A new analytical method was developed for the determination of oxygen isotope ratios in peroxides in rainwater. In the method, rainwater samples were quantitatively degassed of dissolved air by a combined treatment of evacuation, ultrasonic agitation, and helium sparging (VUS), followed by a permanganate oxidation of the dissolved peroxide to O_2. The O_2 was then quantitatively removed from the rainwater by the VUS treatment and converted to CO_2 for mass spectrometric analysis. Using this method, 14 rainwater samples collected at four sites (Argonne, IL, Research Triangle Park, NC, Whiteface Mountain, NY and Dearborn, MI) were analyzed to determinne the fraction of the sulfate in the samples that was produced as a result of the aqueous-phase reaction of dissolved SO_2 with hydrogen peroxide. It was concluded that 40% or more of the sulfate in the samples was formed by peroxide oxidation.

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ABSTRACT

Oxygen isotope ratio measurements were used to examine the importance of peroxide oxidation of SO_2 to sulfate in the atmosphere. A new analytical method was developed for the determination of oxygen isotope ratios in peroxides (concentrations in the ppb range) in rainwater. According to the method, 20-L samples were quantitatively degassed of dissolved air by a combined treatment of evacuation, ultrasonic agitation, and helium sparging (VUS), followed by permanganate oxidation of the dissolved peroxide to O_2; the O_2 was then quantitatively removed from the rainwater by the VUS treatment and converted to CO_2 for mass spectrometric analysis. Stock solutions of H_2O_2 of various ^{18}O enrichments were prepared by a high-voltage discharge method; and, by using these solutions to oxidize SO_2 to SO_4^{2-}, the following isotopic relationship was established:

$$\delta^{18}O_{SO_4^{2-}} = 0.57\,\delta^{18}O_{SO_4^{2-}} + 0.43\,\delta^{18}O_{H_2O} + 8.4‰.$$

This relationship was used to calculate the $\delta^{18}O_{SO_4^{2-}}$ formed by peroxide oxidation and a similar previously established relationship was used to calculate the $\delta^{18}O_{SO_4^{2-}}$ formed by metal-catalyzed aqueous oxidation. These sets of calculated values were compared to the measured values for evaluation of the estimated fraction of sulfate in rainwater that was formed by peroxide oxidation, assuming that metal (or carbon) catalysis was the only other major sulfate formation mechanism. It was concluded that ~40% or more of the sulfate in summer rains in the northeastern U. S. was formed by peroxide oxidation.

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SECTION 1

INTRODUCTION

Considerable interest has been shown in the possibility of using oxygen isotopy to elucidate the role of H_2O_2 in the oxidation of SO_2 to sulfates in the atmosphere. The potential importance of H_2O_2 lies in the view that aqueous-phase oxidation of SO_2 to H_2SO_4 probably accounts for a major fraction of the observed SO_4^{2-} in the precipitation occurring in the northeastern United States. The key reactants responsible for this oxidation are not well known, although a large number of possible catalysts and oxidants exist in the atmosphere, including carbon, transition metal ions, hydroxyl and organic free radicals, hydrogen peroxide (including organic peroxides) and ozone (Penkett *et al.*, 1979). It has been postulated that the atmospheric oxidation of SO_2 is limited by the availability of these oxidants and catalysts, rather than by the availability of SO_2 itself. This is the so-called phenomenon of non-linearity between the concentration (and, by implication, the emission) of SO_2 in the atmosphere and the conversion of this SO_2 to H_2SO_4. If such is indeed the case, it is important to determine if peroxides have a pivotal role in acid formation and deposition from the atmosphere [oxidation by ozone decreases in significance with decreasing *p*H of the rainwater].

Oxygen isotopic studies are useful in distinguishing between the different oxidation mechanisms effective in the atmosphere. Laboratory simulation of several different atmospheric reaction sequences has shown that the oxygen isotope ratio in the product SO_4^{2-} is uniquely related to the reaction pathway followed in its formation (Holt *et al.*, 1982). It may therefore be possible to determine if the atmospheric hydrogen peroxide is responsible for significant oxidation of SO_2 to sulfate, and if it is this oxidant that limits the aqueous-phase formation of sulfuric acid. The results of these studies could have significant implications for energy technology, particularly if they indicate that, because of the non-linearity in SO_2 conversion discussed above, it may be more important to reduce the

ambient concentrations of peroxides than of SO_2.

In the 1981 JASON Committee Report to the U.S. Department of Energy (Chamberlain *et al.*, 1981), some recommendations for further research were based, at least in part, on our earlier work on SO_2 oxidation by H_2O_2 (Holt *et al.*, 1981). According to our earlier work, the $\delta^{18}O$ [deviation in parts per thousand (‰) of the $^{18}O/^{16}O$ ratio of the sample from that of the standard reference material, Standard Mean Ocean Water (SMOW)] of sulfates produced by H_2O_2 oxidation were significantly lower than the $\delta^{18}O$ of sulfates found in rainwater. However, the $\delta^{18}O$ of the reagent-grade H_2O_2 used in those experiments was not known. The results suggested the need for isotopic analysis of H_2O_2 in dilute solutions, and for a methodology whereby the $\delta^{18}O$ values of H_2O_2, H_2O, and SO_4^{2-} in rainwater could be compared, in order to assess the importance of H_2O_2 in the formation of sulfate-constituted acid rain.

The plan of this investigation was to develop a method for the determination of the $\delta^{18}O$ of H_2O_2 in dilute aqueous solutions (simulating rainwater); to prepare solutions of H_2O_2 of various ^{18}O enrichments; to use the freshly prepared solutions of H_2O_2 to oxidize SO_2 to SO_4^{2-} for evaluation of the relationship between $\delta^{18}O_{SO_4^{2-}}$ and $\delta^{18}O_{H_2O_2}$; and to apply this relationship to the measured $\delta^{18}O_{H_2O_2}$, $\delta^{18}O_{SO_4^{2-}}$, and $\delta^{18}O_{H_2O}$ in precipitation water, for assessment of the importance of H_2O_2 in the atmospheric transformation of SO_2 to sulfate.

SECTION 2

EXPERIMENTAL

Development of Analytical Method

No suitable analytical method was available for the quantitative extraction of the oxygen in H_2O_2, (dissolved in water, ppb range), for isotopic analysis. Figure 1 shows a 4-step method which we developed for this purpose. It consists of the removal of dissolved O_2 from 20-liter samples of water by a combination of evacuation, ultrasonic agitation, and sparging with helium; oxidation of the dissolved H_2O_2 to O_2 in the water with $KMnO_4$; removal of the newly formed O_2 from the water in a carrier-gas stream; and conversion of the O_2 to CO_2 by reaction with platinum-catalyzed carbon at 600°C. The CO_2 is then mass spectrometrically analyzed to determine its $\delta^{18}O$ (identical to that of the oxygen in the original H_2O_2).

Analytical Train. Diagrams of the apparatus are shown in Figs. 2 and 3. Fig. 2 shows the all-glass analytical train. It consists of a bed of molecular sieve at −196°C for the removal of traces of O_2 from helium carrier gas, a gas pipet for the injection of known amounts of O_2 or CO_2 into the carrier gas stream during standardization, the water sample chamber detailed in Fig. 3, a 20-mm o.d. cold trap at −78°C for the removal of residual water vapor from the gas stream, a cold trap at −196°C for the removal of CO_2 that is scrubbed from the water sample by the helium stream, a bed of activated charcoal (3 g, 8–10 mesh, coconut grade, in a vertically mounted quartz tube, lined with platinum gauze) at 600°C for the conversion of O_2 to CO_2 in the carrier gas stream, another cold trap at −196°C for the collection of the newly formed CO_2 from the gas stream, a capillary open-well mercury manometer for measurement of the CO_2, and a gas sample bulb, attached to the train for transfer of the CO_2 to a mass spectrometer for isotopic analysis. A cold trap at −196°C, not shown in the diagram, is in the vacuum manifold to protect the analytical train from vapor contamination from the mechanical vacuum pump.

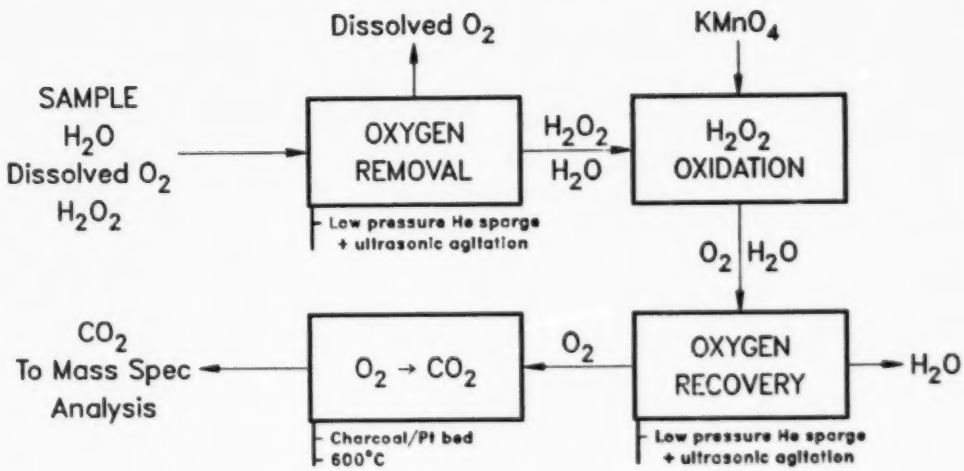

Figure 1. **Four-step method for conversion of oxygen in H_2O_2 (ppb range in water) to CO_2 for mass spectrometric analysis**

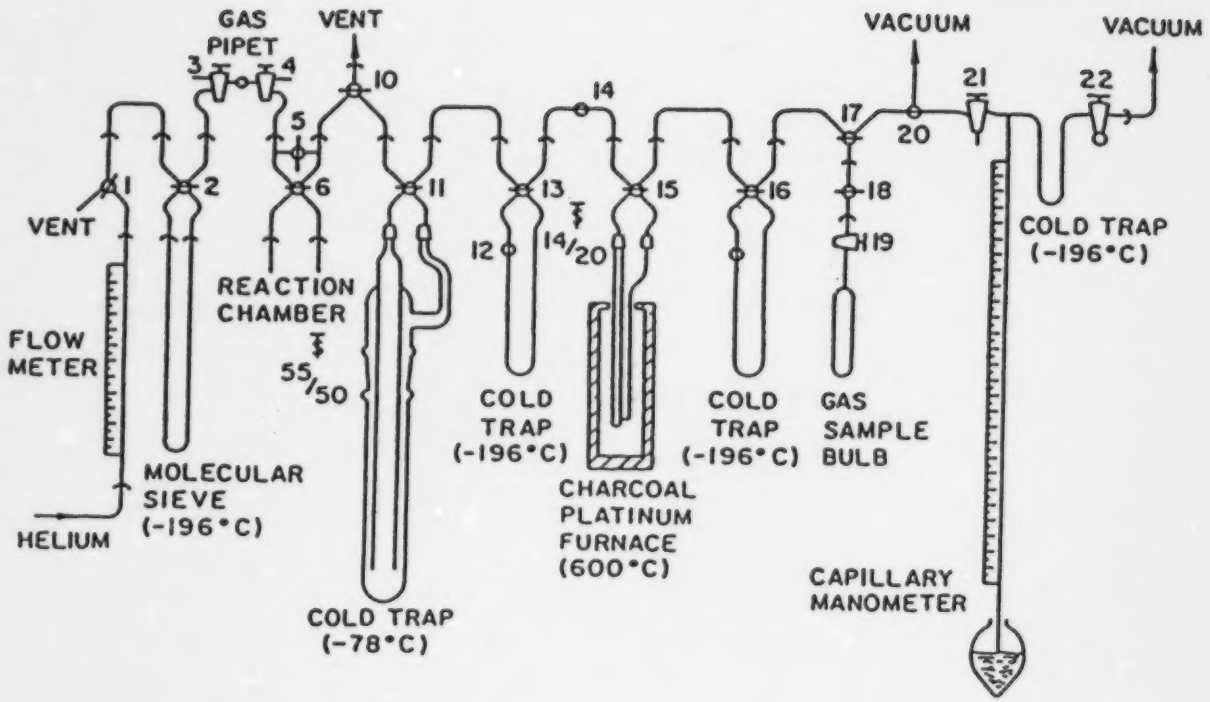

Figure 2. Analytical train

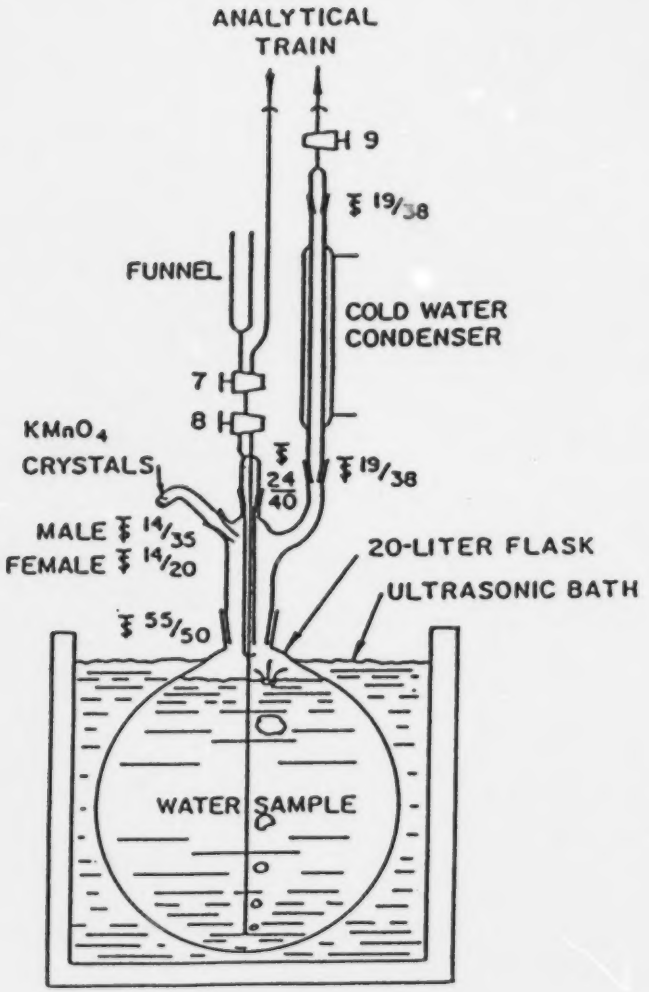

Figure 3. Reaction chamber

Reaction Chamber. The reaction chamber assembly, Fig. 3, consists of a 20-L round bottom flask, a rotatable side-arm tube for the addition of crystalline $KMnO_4$, a cold water condenser to limit the amount of water vapor swept by the helium stream into the −78°C cold trap, three stopcocks for manipulation of the helium stream, and a funnel for the addition of solutions of acid and oxidants (used only during the development of the method). The round-bottom flask was supported by a stainless steel rack in an 83-L stainless-steel tank, interior 40.6 × 50.8 × 40.6 cm, (Model ATH 1620-24), of an ultrasonic cleaning system (Model EMa 50-24) manufactured by Branson Cleaning Equipment Co., Shelton, CT. The water in the ultrasonic tank was maintained at about 10°C by circulation through a refrigeration unit.

The components of the glass analytical train were connected by No. 18 ball joints, sealed with solidified black wax. The hollow plug of stopcock 22 was modified to provide extra volume in the capillary manometer (Holt, 1955).

Conversion of O_2 to CO_2. The first part of the method to be developed was the conversion of O_2 to CO_2 in the carrier gas stream (4th box in the flow sheet, Fig. 1). The procedure is a modification of an established vacuum technique for the conversion of oxygen in air to CO_2 for mass spectrometric analysis. By the vacuum procedure, the air is circulated at low pressure over graphite and platinum at 600°C and the resulting CO_2 is cryogenically removed from the closed system (Horibe *et al.*, 1973; Holt, 1977). By our new method, in which helium is conducted through a bed of 8–10 mesh activated coconut charcoal at 600°C and in contact with platinum gauze, the yield of CO_2 was found to be affected by both the bed temperature and the axial temperature gradient. With a suitably long furnace to obtain an essentially isothermal bed, the recovery of O_2 (as CO_2) as a function of bed temperature is shown in Fig. 4. The data show that the optimum bed temperature for maximum yield of CO_2 was ~600°C, the same as that used by Horibe

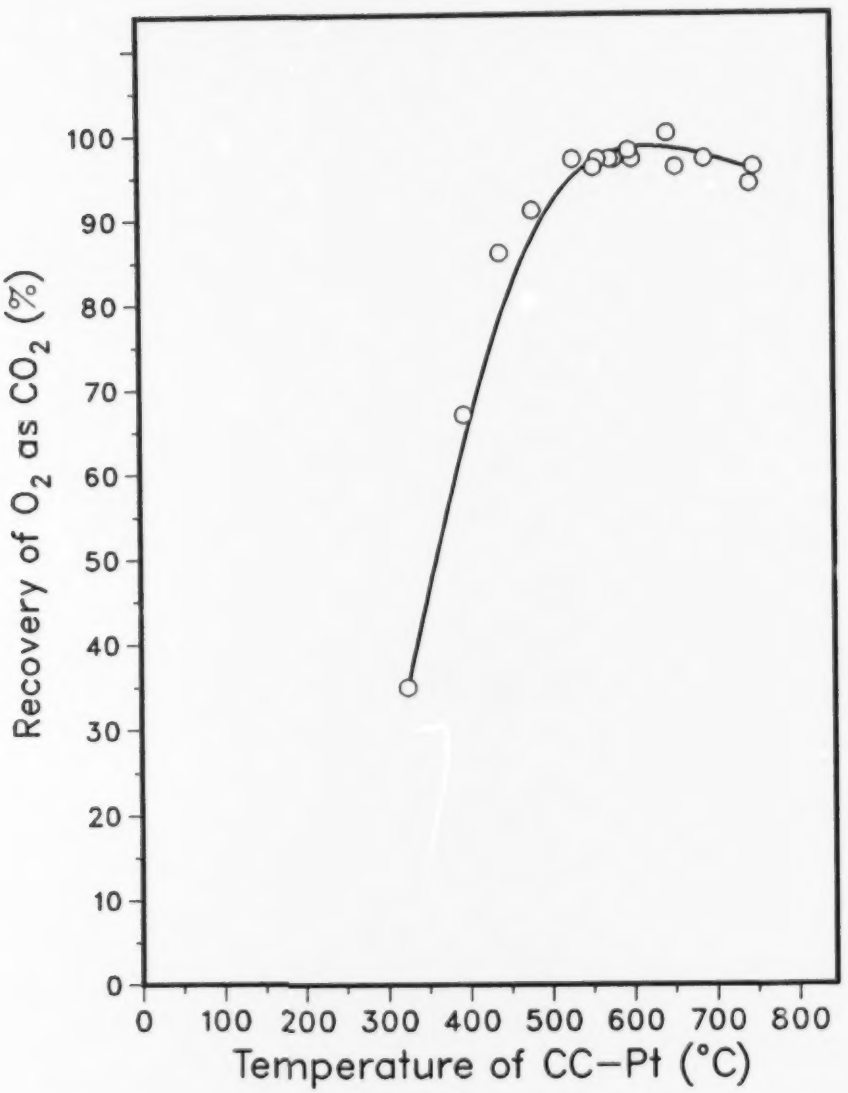

Figure 4. Recovery of O_2 as CO_2 after reaction with charcoal in contact with platinum at various temperatures

et al., (1973) and Holt (1977) in vacuum-line applications.

The data in Fig. 4 also indicate that the maximum recovery of the added O_2, measured as CO_2, was ~97%. Recoveries higher than 97% were apparently unattainable because of competing reactions. At temperatures lower than 600°C, the formation of CO_2 was decreased due to the incomplete reaction,

$$O_2 + C \rightarrow CO_2 \qquad (1)$$

and at higher temperatures, the yield of CO_2 was decreased by the competing reaction,

$$CO_2 + C \rightarrow 2CO. \qquad (2)$$

The effect of reaction (2) was demonstrated by injecting CO_2 into the carrier gas instead of O_2. The results, Fig. 5, confirm that about 3% of the CO_2 decomposed at 600°C.

The 97% recovery is adequate for isotopic studies; and, at 600°C, oxygen isotope fractionation within the equilibrated system of CO_2, CO, unconverted CO_2, and fixed oxygen on the charcoal is negligible. The demonstrated reliability of the 97% recovery at 600°C allows the applicability of the technique to the quantitative determination of O_2 in gas streams, as well as to isotopic studies.

Removal of Dissolved O_2 from Water

After it was experimentally demonstrated that O_2 could be reliably converted to CO_2 in a carrier-gas stream, the technique for the quantitative removal of dissolved oxygen from multi-liter quantities of water was developed (1st and 3rd boxes in Fig. 1). Various combinations of sparging with helium, vacuum pumping, and ultrasonic agitation were tested. The best results were obtained by a combination of all three. (The commonly used degassing method of alternately freezing and thawing the water under vacuum was much too impractical and time-consuming for large samples of water.)

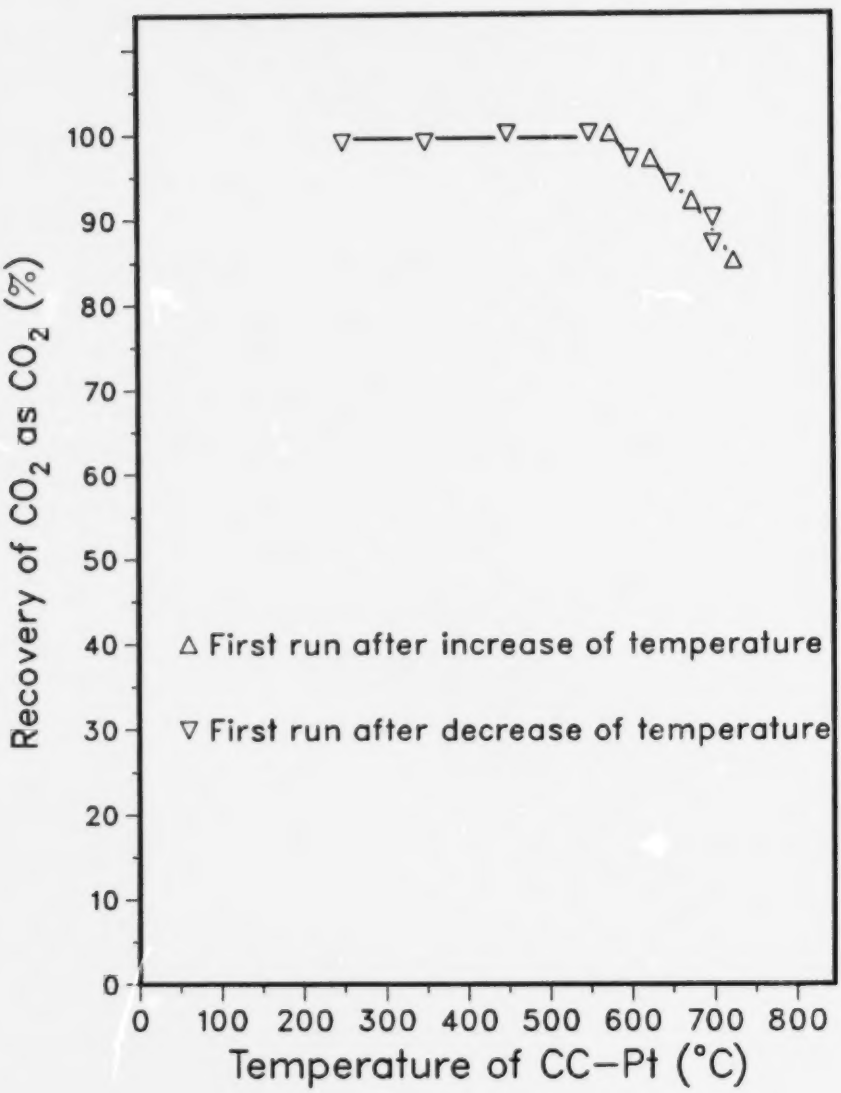

Figure 5. Recovery of CO_2 after exposure to charcoal and platinum at various temperatures

Helium Sparge. Attempts were made at first to remove dissolved oxygen from water (saturated with air) by only sparging with helium. Quantitative removal of air oxygen from the water by this technique was intolerably slow. Curve SP-1 in Fig. 6 shows the percent removal of O_2 (estimated to be dissolved in the air-saturated water at room temperature) plotted vs. minutes of sparging. After 50 min of sparging, only ~1/3 of the dissolved O_2 had been removed.

T. G. Holt (1983) cited a comparison of various degassing techniques in Technical Brief No. 101 of Waters Associates, Milford, Massachusetts. The techniques, listed in the order of decreasing effectiveness for the removal of dissolved gases from liquids, were: (1) vacuum pumping combined with ultrasonic agitation, (2) vacuum filtration using a Waters Solvent Clarification Kit, (3) ultrasonic agitation, (4) vacuum pumping, (5) boiling, and (6) sparging.

Vacuum-Ultrasonic Agitation (VU). The apparatus was arranged to accommodate treatment of the water sample by a combination of vacuum pumping and ultrasonic agitation. The results of two experiments, VU-1 and VU-2, are plotted in Fig. 6. The rate of removal of dissolved oxygen was found to be greatly enhanced by "rinsing" the water with helium. That is, the evacuated sample chamber was filled with pure helium to atmospheric pressure by allowing the gas to bubble through the water; then it was exhausted through the analytical train. The sequential dissolution and removal of the helium from the water had the effect of "rinsing" the O_2 from the water. Curve VUR-1 in Fig. 6 shows the improved results of a third experiment in which the water sample was rinsed with He at regular intervals throughout the O_2-removal treatment.

Vacuum-Ultrasonication-Sparging (VUS). The improved rate of O_2 removal by frequently rinsing the O_2 from the water with helium suggested that a low-pressure sparge by helium should be combined with the vacuum-ultrasonic agitation treatment. This technique, tested in runs VUS-1, VUS-2, VUS-3, and VUS-4 yielded the best O_2 removal rates.

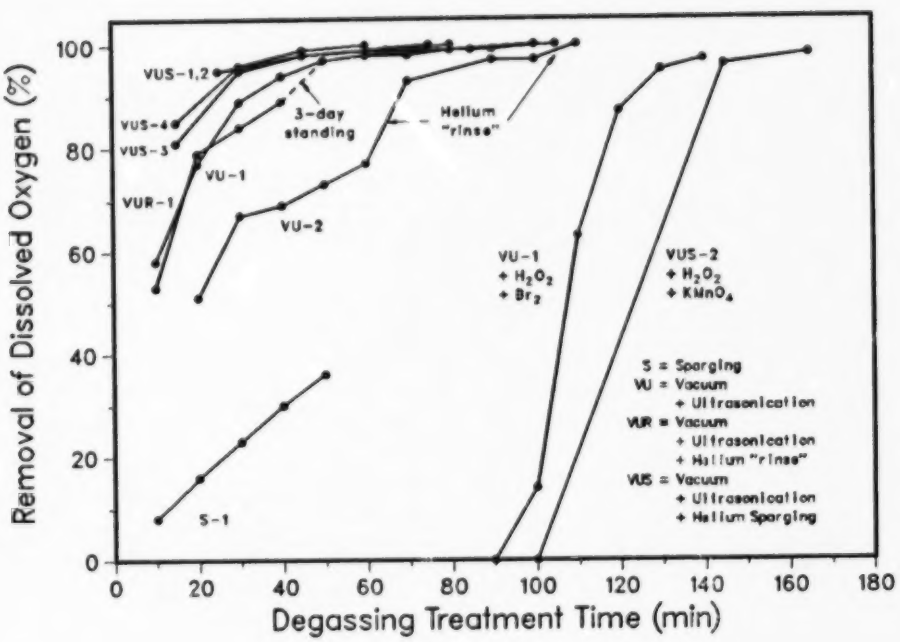

Figure 6. Removal of O_2 from water by various degassing techniques

The results show removal of ~99% of the dissolved oxygen in 1 h of VUS for 3-L water samples. (20-liter samples were later found to require ~5 h of the treatment for complete air removal.)

Oxidation of H_2O_2 to O_2 in Water

Bromine water was tested as an oxidant of H_2O_2 to O_2 in the degassed water sample. Although it was very effective in converting a known amount of H_2O_2 to O_2, its use was complicated by its exposure to stopcock grease and by contamination of the analytical train. Curve "VU-1 + H_2O_2 + Br_2" in Fig. 6 shows the results of one experiment in which a degassed water sample (VU-1) was spiked with H_2O_2 and treated with bromine water, yielding a recovery of about 97% in 50 min of VU treatment.

Potassium permanganate was used in all subsequent experiments. Curve "VUS-2 + H_2O_2 + $KMnO_4$" in Fig. 6 shows the results of an experiment made to compare its effectiveness to that of bromine. The recovery of oxygen, added as H_2O_2 to a degassed water sample (see curve VUS-2), was also ~97% after 1 h of vacuum ultrasonic sparging. In earlier experiments with $KMnO_4$, it was added as a 0.1N solution through the funnel, Fig. 3; later, the rotatable side arm was made a part of the apparatus to permit the addition of $KMnO_4$ crystals, with correspondingly lower procedure blanks.

Synthesis of ^{18}O-enriched H_2O_2

Hydrogen peroxides of various $\delta^{18}O$ were not commercially available. A suitable method of synthesis (Vol'nov *et al.*, 1964) was identified and successfully applied to the laboratory preparations of four stock solutions of H_2O_2 of different $\delta^{18}O$. By this method, H_2O_2 is formed by exposure of supplies of water vapor, each differing in $\delta^{18}O$, to a high-voltage (~1.4 kV) discharge in ~100 cm of 10-mm o.d. glass tubing between two water-

cooled aluminum electrodes. Some of the HO radicals, formed by the dissociative reaction,

$$2H_2O \rightleftarrows 2HO + 2H \qquad (3)$$

are condensed in a cold trap (−196°C) where they combine to form H_2O_2, leaving the H radicals to combine in formation of H_2 and be pumped away through the vacuum line.

Other techniques which we experimentally found to give inadequate yields of H_2O_2 were conduction of an electric arc across a stream of aerosolized water droplets (Kok, 1982), excitation of water vapor by a radio-frequency silent discharge in a glass chamber (7.5 cm dia × 20 cm long) in a commercially available plasma cleaner unit, and excitation by a glow-discharge unit (4.8 cm dia × 70 cm long) that had uncooled aluminum disk electrodes (Jarnagin and Wang, 1958).

Collection of Rain Samples

Each rain sampling station consisted of four 1-m^2 plastic skylights, inverted to form funnels and fitted with plastic nipples and hoses to allow the water to flow into two 25-L plastic collection bottles. From each collected sample of >29-L, a 4-L bottle was filled for subsequent determination of $\delta^{18}O_{H_2O}$ and $\delta^{18}O_{SO_4^{2-}}$, and a 25-L bottle was filled for subsequent determination of $\delta^{18}O_{H_2O_2}$. The 4-L sample was treated with 20 mg CuCl to prevent bacterial alteration of the sulfate during storage before analysis; the 25-L sample was treated with 25 ml concentrated H_2SO_4 and was refrigerated at ~5°C to prevent autodecomposition of the H_2O_2 during storage before analysis.

During the period June–August 1985, rainwater collection stations, in addition to the one at Argonne, IL, were operated by the Research Engineering Staff, Ford Motor Company, Dearborn, MI; Research Triangle Institute, Research Triangle Park, NC; and Whiteface Mountain Field Station, State University of New York, Albany, NY. Approximately two rain events per month were sampled at each site during the 3-month period.

The rain collectors were installed by GP Engineering, Downers Grove, IL, at each of the three sites. Insulated containers were used for shipment of 25-L bottles of acidified, chilled rainwater by air express to Argonne for analyses.

SECTION 3

RESULTS

Recovery of added H_2O_2

The recovery of reagent grade H_2O_2, added to 20 liters of distilled water, was about 96%. This recovery is adequate for determining the oxygen isotope ratio and the concentration of H_2O_2 in rainwater.

Test for Isotopic Interference

Schumb *et al.* (1955) cite references showing that dissolved H_2O_2 does not exchange oxygen atoms with the solvent water, dissolved molecular oxygen, or oxygenated products. In decomposition of H_2O_2 by oxidation to molecular oxygen, the O–O bond is not broken and no fractionation occurs. The MnO_4^- ion does not cause isotopic interference (Cahill and Taube, 1952). However, in decomposition of H_2O_2 by reduction (not applicable to our experimentation), the bond is severed and fractionation may occur.

To confirm the absence of appreciable isotopic interference in our procedure by oxygen exchange between the H_2O and either the H_2O_2 or the O_2, before, during, or after the oxidation reactions, the oxidation was carried out in the presence of three different water supplies of various $\delta^{18}O$. The results in Fig. 7 show that the $\delta^{18}O$ of the CO_2 product was unaffected by the $\delta^{18}O$ of the water solvent.

Effects of Autodecomposition of H_2O_2

Results from two sets of experiments on the autodecomposition of H_2O_2 (spikes added to 20-L samples of rainwater), over storage times of up to 11 days, showed that if the rainwater is stored unacidified at room temperature, the H_2O_2 concentration declines rapidly (~30% depletion in 2 days and ~98% in 11 days); and that the $\delta^{18}O$ of the

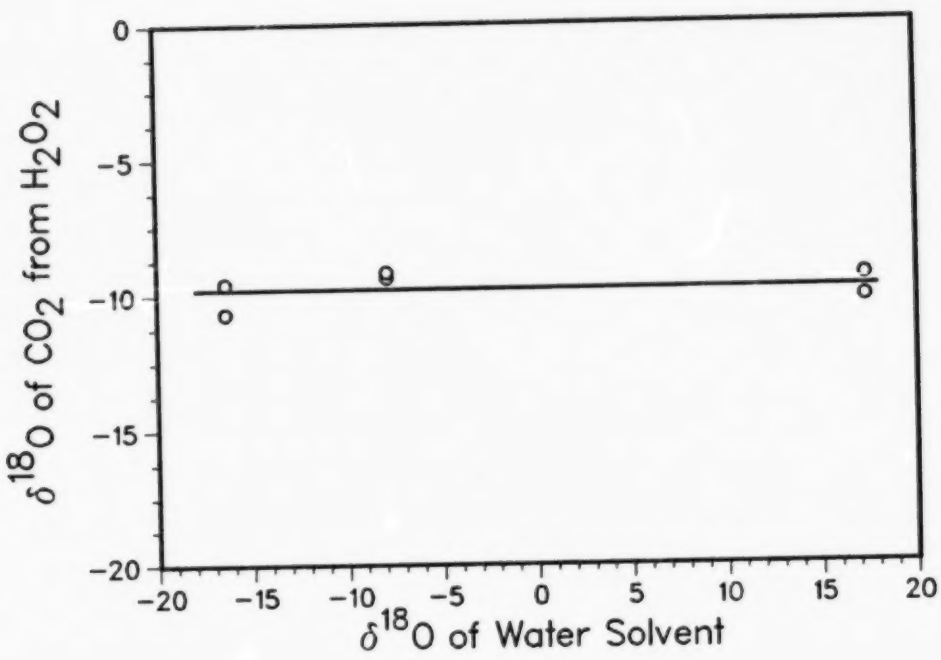

Figure 7. Isotopic effects of water solvent on the $\delta^{18}O$ of CO_2 originating from H_2O_2

undecomposed H_2O_2 undergoes a corresponding increase (~5‰ during the first 5 days). However, if the rainwater is first acidified (~20 ml conc. H_2SO_4 in 20-L) and kept cold (1–9°C) during storage, the changes in the concentration and in the $\delta^{18}O$ of the H_2O_2 are negligible.

Effects of $KMnO_4$ Decomposition

Decomposition of excess $KMnO_4$ by organic matter in rainwater was shown to produce only CO_2, which is cryogenically removed in the analytical train before the H_2O_2-derived O_2 is converted to CO_2. The reaction between $KMnO_4$ and organic matter does not produce O_2 and is therefore not a source of interference in the method.

Procedure Blank

The blank of the analytical procedure was reduced from 6.5 to 3.5 μmoles of O_2 by adding the $KMnO_4$ to the 20-L sample as pulverized crystals rather than as a pre-boiled $KMnO_4$ solution. (In 20-L of water, 3.5 μmoles is ~3 ppb.)

Isotopic Relationships

High-Voltage Preparation of H_2O_2 from H_2O. The dependence of the $\delta^{18}O$ of H_2O_2 on the $\delta^{18}O$ of the H_2O from which it was prepared by the high-voltage discharge method described above is shown in Fig. 8. The equation of the best fit regression curve is

$$\delta^{18}O_{H_2O_2} = 1.03\delta^{18}O_{H_2O} + 29.4‰. \quad (4)$$

The results indicate that the $\delta^{18}O_{H_2O_2}$ is controlled directly by the $\delta^{18}O$ of the H_2O and that the $\delta^{18}O$ of the H_2O_2 is substantially higher (~29‰) than that of the water from which it was formed. Although the high-voltage process used in these preparations

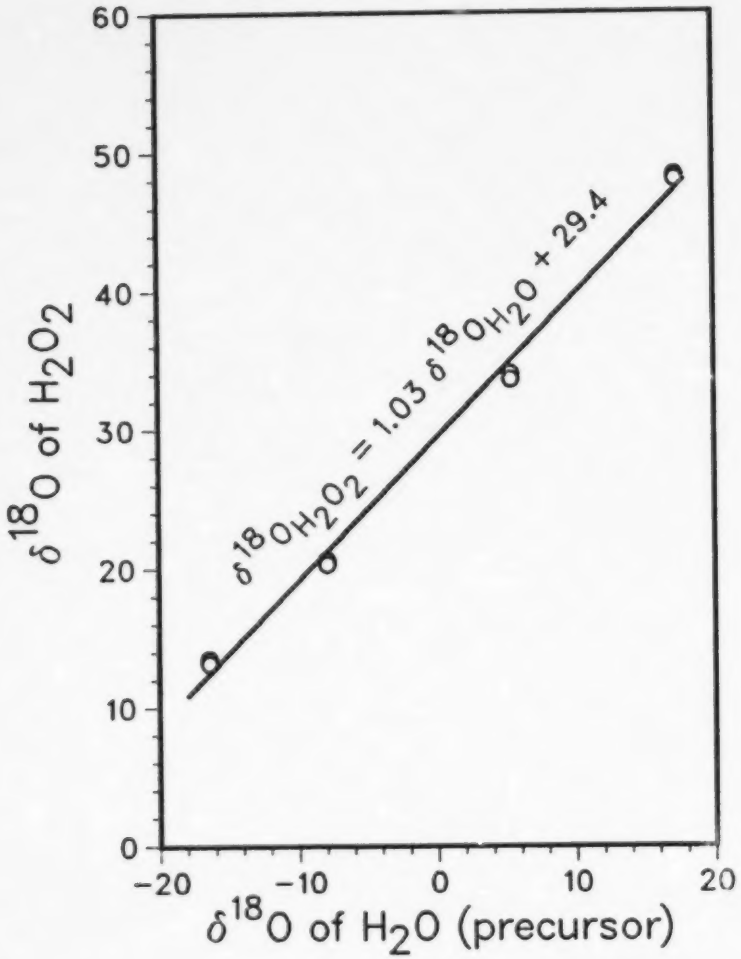

Figure 8. Dependence of $\delta^{18}O_{H_2O_2}$ on $\delta^{18}O_{H_2O}$ in a high-voltage discharge process of formation

of H_2O_2 may simulate lightning in the atmosphere, the importance of lightning, relative to other sources of H_2O_2 in the atmosphere, is open to question (Kok, 1982).

H_2O_2 Oxidation of SO_2 to SO_4^{2-}. Using the four stock solutions of hydrogen peroxide, each of different $\delta^{18}O$, sulfate solutions of correspondingly different $\delta^{18}O$ were prepared by oxidation of SO_2 which was in isotopic equilibrium with water of constant $\delta^{18}O = -7.9‰$. In Fig. 9 the $\delta^{18}O$ of each resulting sulfate is plotted versus the $\delta^{18}O$ of the H_2O_2 and the equation of the best-fit regression curve is

$$\delta^{18}O_{SO_4^{2-}} = 0.43\ \delta^{18}O_{H_2O_2} + 3.5‰. \tag{5}$$

The regression curve of the previously determined relationship (Holt *et al.*, 1981) between $\delta^{18}O_{SO_4^{2-}}$ and $\delta^{18}O_{H_2O}$ in aqueous-phase oxidation of SO_2 by H_2O_2 was

$$\delta^{18}O_{SO_4^{2-}} = 0.57\ \delta^{18}O_{H_2O} - 2.4‰. \tag{6}$$

Assuming that all significant effects of the $\delta^{18}O$ of the SO_2 on the $\delta^{18}O$ of the SO_4^{2-} are lost by rapid isotopic exchange between the SO_2 and the large excess of water, prior to appreciable oxidation (Holt *et al.*, 1981), $\delta^{18}O_{H_2O}$ and $\delta^{18}O_{H_2O_2}$ remain as the only two complementary variables in the equation for $\delta^{18}O_{SO_4^{2-}}$; therefore, the comprehensive regression curve for $\delta^{18}O_{SO_4^{2-}}$ is

$$\delta^{18}O_{SO_4^{2-}} = 0.57\ \delta^{18}O_{H_2O} + 0.43\ \delta^{18}O_{H_2O_2} + C \tag{7}$$

$$= \sim\frac{3}{5}\ \delta^{18}O_{H_2O} + \sim\frac{2}{5}\ \delta^{18}O_{H_2O_2} + C. \tag{8}$$

The constant, C, was evaluated at 8.4‰ from the data given in Fig. 9 by substituting the corresponding measured values for $\delta^{18}O_{SO_4^{2-}}$ and $\delta^{18}O_{H_2O_2}$, and $-7.9‰$ for $\delta^{18}O_{H_2O}$.

The comprehensive equation then becomes

$$\delta^{18}O_{SO_4^{2-}} = 0.57\ \delta^{18}O_{H_2O} + 0.43\ \delta^{18}O_{H_2O_2} + 8.4‰ \tag{9}$$

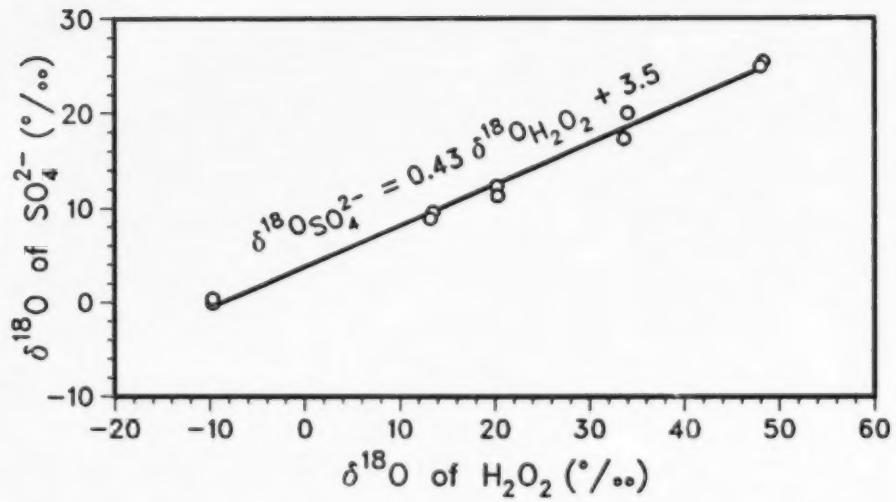

Figure 9. Dependence of $\delta^{18}O_{SO_4^{2-}}$ on $\delta^{18}O_{H_2O_2}$ in oxidation of SO_2 to SO_4^{2-}

and can be used to calculate $\delta^{18}O_{SO_4^{2-}}$ from $\delta^{18}O_{H_2O_2}$ and $\delta^{18}O_{H_2O}$ of rainwater for comparison with corresponding measured values of $\delta^{18}O_{SO_4^{2-}}$. This comparison may prove to be uniquely useful in the assessment of the importance of H_2O_2 in the oxidation of SO_2 to SO_4^{2-} in the atmosphere.

The slope of 0.43 (approximately 2/5) in Eq. (5) of the regression curve through the data of Fig. 9 confirms the evidence of the intermediate species, $H_2O_2 \cdot SO_3^{2-}$, which was previously proposed (Holt *et al.*, 1981). Apparently, the $\delta^{18}O$ of the sulfate product is 2/5-controlled by the two oxygens in the H_2O_2 of the adduct, and 3/5-controlled by the HSO_3^-, which, in turn, is isotopically controlled by rapid oxygen exchange with the large excess of water with which it is associated.

$\delta^{18}O$ and Concentration of H_2O_2 in Rainwater

Forty-four samples of rainwater, collected at Argonne from September 1984 through November 1985 and at the other three sites (in Michigan, New York, and North Carolina) during the summer months of 1985, were analyzed by the new method. Results obtained for 14 of these samples are given in Table 1 and in Fig. 10. Isotopic data for H_2O, SO_4^{2-}, and H_2O_2 in rainwater from the four sites are plotted vs. time in Fig. 10; in addition, Table 1 gives concentrations of H_2O_2 and SO_4^{2-} in the rainwater, and the elapsed time between collection and analysis of each sample. Our analytical method does not discriminate H_2O_2 from organic peroxides in rainwater; consequently, in the report of field results and in the discussions that follow, "H_2O_2" will refer to combined H_2O_2 and other active peroxides.

Results for 25 of the samples are not reported because the concentrations of H_2O_2 were too low (<15 ppb) to yield sufficient amounts of CO_2 to give reliable isotopic data by mass spectrometric analysis. Discarding of these samples of low H_2O_2 concentration has the effect of estimating a lower than actual proportion of sulfate formed by peroxide oxidation of SO_2 discussed later in the report. [The cause(s) of very low peroxide concentrations in rainwater samples may be one or more of the following: (1) during early use of the method,

Table I.

Concentration and isotopic results for rainwater collected at Argonne National Laboratory, IL, (ANL); Dearborn, MI, (DEA); Whiteface Mountain, NY, (WFM); and Research Triangle Park, NC, (RTP); May–September, 1985.

		Concentration		$\delta^{18}O$		
Sample No.	Storage (days)	H_2O_2 (ppb)	SO_4^{2-} (mg L^{-1})	H_2O_2 (‰)	H_2O (‰)	SO_4^{2-} (‰)
ANL–5/27/85	2	330	2.4	44.8	−3.1	15.8
WFM–6/07/85	6	124	1.5	50.5	−3.7	15.0
RTP–6/12/85	6	147	2.4	47.5	−3.5	14.4
RTP–6/18/85	9	374	2.1	45.0	−2.5	15.8
ANL–7/02/85	7	316	2.1	41.4	−3.1	12.6
DEA–7/02/85	9	23	4.4	58.3	−6.6	12.9
ANL–7/09/85	7	90	4.4	54.2	−1.0	16.9
RTP–7/10/85	8	433	3.6	53.8	−2.6	14.3
WFM–7/15/85	17	201	2.0	48.4	−3.9	15.3
RTP–7/16/85	20	224	3.6	58.0	−1.5	16.4
WFM–7/31/85	64	160	1.2	41.0	−7.9	14.1
DEA–8/14/85	127	16	2.9	47.9	−1.3	16.8
RTP–8/20/85	79	184	4.1	49.6	−3.5	12.8
ANL–9/06/85	76	33	1.2	44.8	+0.4	16.1

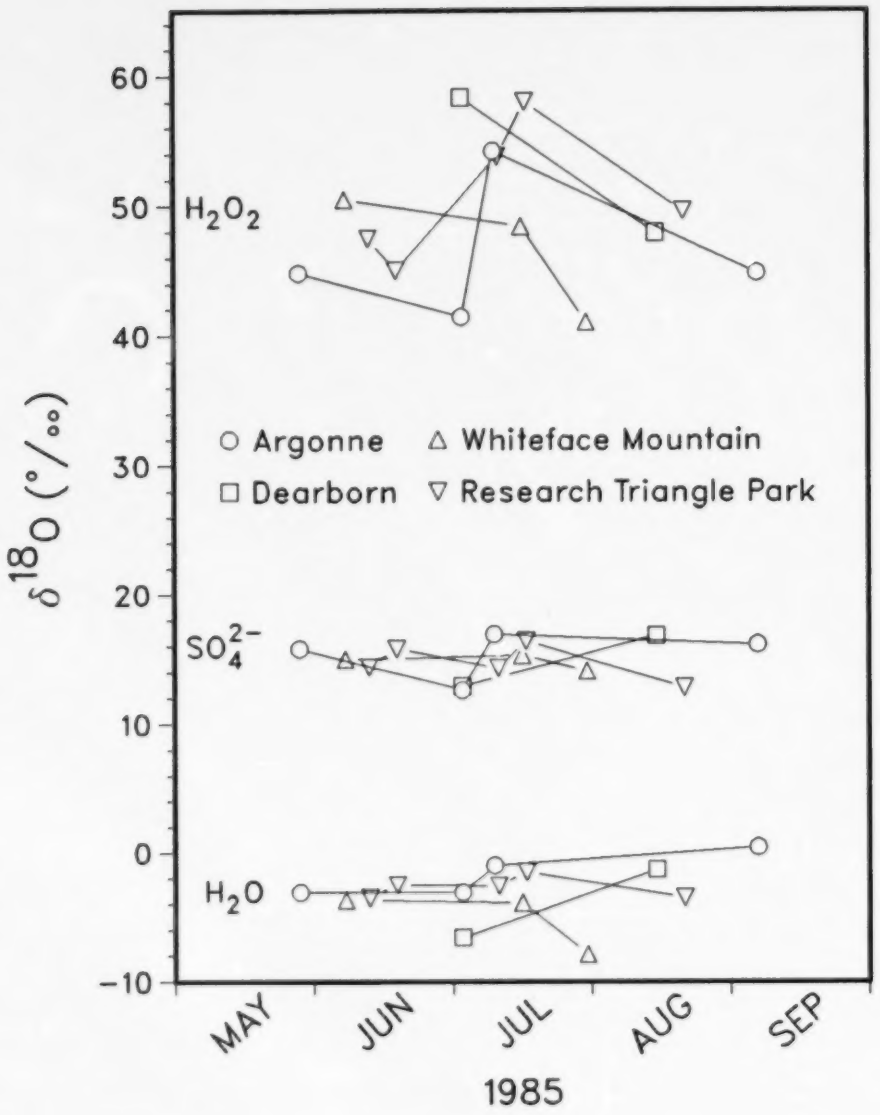

Figure 10. Measured isotopic data for H_2O_2, SO_4^{2-}, and H_2O in the samples of rainwater

storage procedures were inadequate for prevention of autodecomposition of peroxides; (2) several samples were collected during winter months of 1984–85 when concentrations of peroxides in precipitation were very low, and (3) high concentrations of SO_2, relative to peroxides, in the atmosphere depletes the peroxide that might otherwise be present in collected samples of rainwater.] Similarly, three samples were disqualified because of very low sulfate concentrations (<0.3 mg L^{-1}), and the data for two other samples were not included because of analytical difficulties (back diffusion of CO_2 from the charcoal furnace into cold trap 2, when the line was inadvertently evacuated between the furnace and the water sample with no helium flow).

SECTION 4

DISCUSSION

$\delta^{18}O$ of H_2O_2 in Rainwater

A unique characteristic of atmospheric peroxides, as shown for the first time by application of our newly developed analytical method, is the very high $\delta^{18}O$, relative to the $\delta^{18}O$ of atmospheric water, sulfates, and air. As demonstrated in Fig. 10, the measured $\delta^{18}O$ of atmospheric peroxides ranged from 45 to 60‰; sulfates, 13 to 17‰; and rainwater 0 to −6‰. (The $\delta^{18}O$ of air oxygen is constant at 23.5‰.) In contrast to the very high $\delta^{18}O$ of atmospheric peroxides, the $\delta^{18}O$ of reagent-bottle H_2O_2 (Fisher Scientific, H325) was found to be −6‰.

The oxygen isotopy of peroxide formation in the atmosphere, resulting in such high $\delta^{18}O$, is intriguing because it is necessarily related to the mechanism(s) by which the peroxide is formed. For the various sources of atmospheric peroxides (Lee, 1985), each possible mechanism of formation is characterized by its own oxygen isotopy. Consequently, our results suggest that oxygen isotopic studies may well be uniquely applicable to investigations of the origin of peroxides in the atmosphere.

As mentioned earlier, the $\delta^{18}O$ of peroxides in rainwater was higher than might be expected for H_2O_2 that is formed by high-voltage discharge, such as lightning. For example, application of Eq. 4 to the range of $\delta^{18}O$ in water (Fig. 10) would lead to an estimated range for H_2O_2 of ~24‰ instead of the observed 45–60‰.

A phenomenon that may contribute substantially to the relatively high $\delta^{18}O$ of peroxides in rainwater (depending on the conditions of the rainfall, the sample collection, and the storage) is autodecomposition of the peroxide. As the peroxides decompose (under favorable conditions of catalyzing contaminates, temperature and pH), the $\delta^{18}O$ by the residual peroxides is expected to increase. Therefore, depending on the extent of autodecomposition between the time of liquid-phase oxidation of SO_2 in the atmosphere and the

time of collection, acidification, and refrigeration on the ground, the $\delta^{18}O$ of the residual H_2O_2 in the analyzed sample may be significantly higher than that of the H_2O_2 involved in the SO_2 oxidation. Further experimentation to establish the relationship between the $\delta^{18}O$ of peroxide in cloud water and that of concurrently collected rainwater on the ground might provide a correction factor which would improve the significance of the isotope data that is conveniently available from the analysis of water in ground-based collectors.

$\delta^{18}O$ of Atmospheric Sulfates: Measured vs. Calculated

The measured $\delta^{18}O$ values for sulfates, Fig. 10, are co-plotted in Fig. 11 with correspondingly calculated values for H_2O_2 oxidation, metal-catalyzed aqueous oxidation, and primary sulfates. The measured values are clearly higher than those calculated for metal-catalyzed oxidation and clearly lower than those calculated either for H_2O_2 oxidation or for primary sulfates. Calculated values for H_2O_2 oxidation were obtained by use of Eq. (9) for metal-catalyzed aqueous oxidation by

$$\delta^{18}O_{SO_4^{2-}} = 0.8\delta^{18}O_{H_2O} + 10‰ \text{ (Holt } et\ al.\text{, 1982)} \qquad (10)$$

and for primary sulfates by

$$\delta^{18}O_{SO_4^{2-}} = 0.015\delta^{18}O_{H_2O} + 45‰ \text{ (Holt } et\ al.\text{, 1984).} \qquad (11)$$

In 1982, Holt *et al* proposed that since their measured values for $\delta^{18}O_{SO_4^{2-}}$ in precipitation water ranged consistently between the calculated values for primary sulfates and secondary sulfates produced by metal-catalyzed oxidations, the fraction of atmospheric sulfates at a given site originating as primary sulfates, could be estimated. At that time, however, the isotopic qualities of atmospheric peroxides and of the sulfates which they might produce were unknown. Since then field experiments were performed near a strong source of primary sulfates, the isotopic results of which indicated that scavengement was ~300 times more efficient for sulfates than for SO_2 (Holt *et al.*, 1983). Consequently, we expect that, during precipitation, scavengement of primary sulfates is essentially complete

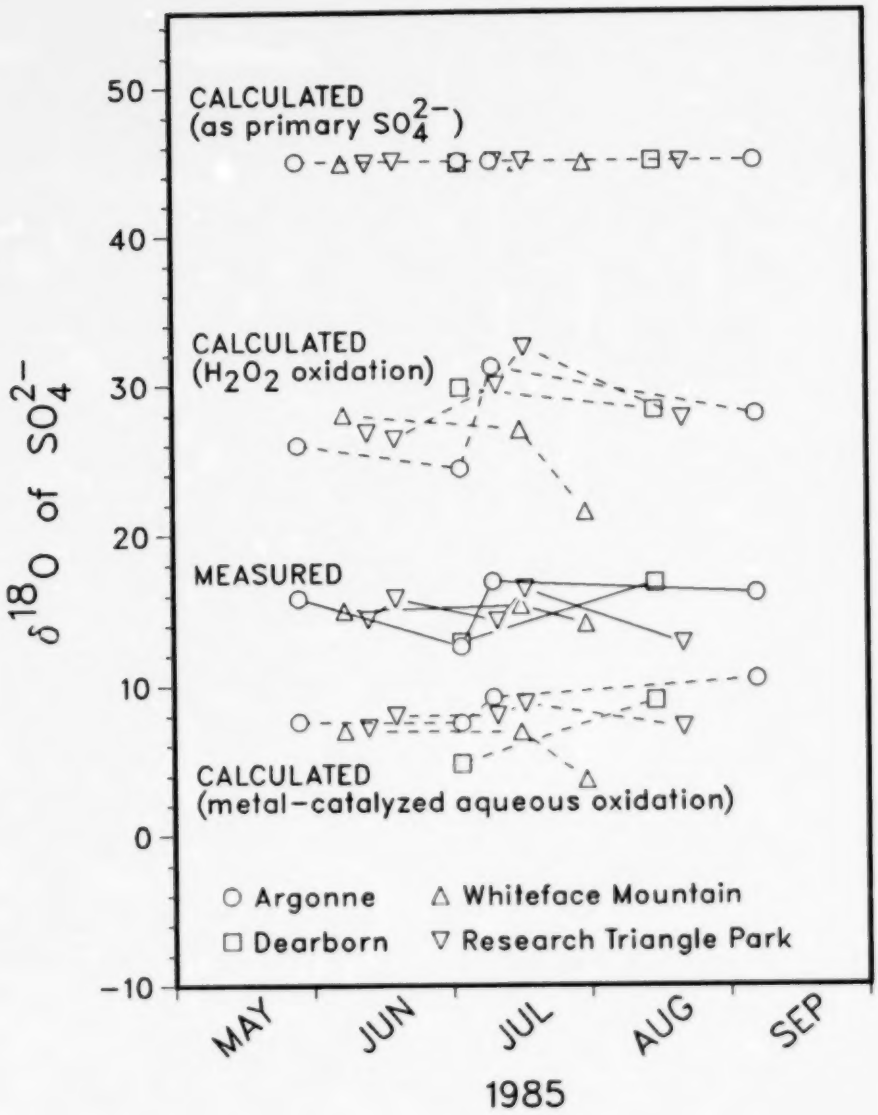

Figure 11. $\delta^{18}O$ of sulfate in rainwater: calculated compared to measured

within a few kilometers of the source, whereas beyond a few kilometers, the scavenged sulfates are mainly secondary sulfates, formed earlier or within the storm system by one or more mechanisms of SO_2 oxidation.

Fraction of Atmospheric Sulfates Formed by Peroxide Oxidation

Assuming that primary sulfates of characteristically high $\delta^{18}O$ (Holt *et al.*, 1984) are effectively scavenged by rain within a short distance from their sources, an estimation of the fraction of sulfates in rainwater several kilometers from a strong source can be made from relative deviations of the measured $\delta^{18}O_{SO_4^{2-}}$ values from the corresponding calculated $\delta^{18}O_{SO_4^{2-}}$ values for peroxide oxidation and metal-catalyzed O_2 oxidation, respectively.

Using the following relationship for calculation of the percentage of sulfate in rainwater formed by H_2O_2 oxidation,

$$(\%) = \frac{\delta^{18}O_{SO_4^{2-}}(\text{meas.}) - \delta^{18}O_{SO_4^{2-}}(\text{calc., } O_2 \text{ oxdn.})}{\delta^{18}O_{SO_4^{2-}}(\text{calc., } H_2O_2 \text{ oxdn.}) - \delta^{18}O_{SO_4^{2-}}(\text{calc., } O_2 \text{ oxdn.})} \times 100, \qquad (12)$$

the percentages for our four sampling sites during 1985 are plotted vs. time in Fig. 12. The average for all of the values at all of the sites is 37 ± 8% sulfate, formed by peroxide oxidation.

Equation (12) assumes that all sulfate measured in the rainwater samples was produced within the raining cloud and that only H_2O_2 and metal-catalyzed aqueous oxidation contributed to the oxidation of the dissolved SO_2. Other potential sources of sulfate in the rainwater samples were aqueous-phase ozone oxidation of SO_2, dissolution after gas-phase reaction of SO_2 with OH radicals, and dissolution of sulfate nuclei previously formed in non-precipitating clouds by any of the above oxidation processes.

In reviewing our work, Dodge (1986) pointed out that the results of other researchers (Scott, 1982; Hegg and Hobbs, 1984; Scire and Venkatram, 1985) variously indicate that 65 to 85% of sulfate in cloudwater is due to *in situ* aqueous phase reactions and the remainder

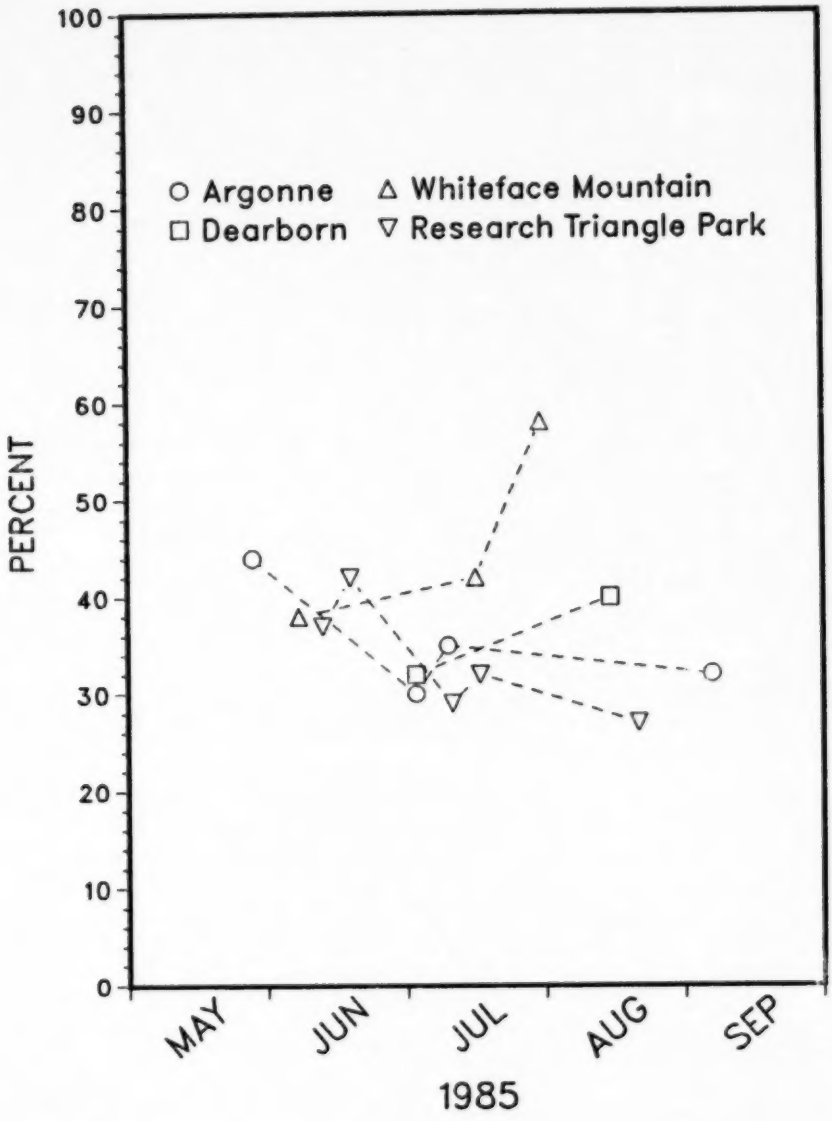

Figure 12. Percent of sulfate formed by peroxide oxidation, assuming negligible primary sulfates

to cloud scavenging of pre-existing sulfates. However, since the residence time of aerosol sulfate in the atmosphere is rather short, any aerosol sulfate scavenged could be expected to be about the same in isotopic quality as that in the precipitating cloud system. Further, ozone is expected to play a minor role in the oxidation of SO_2 in cloudwater of *p*H lower than about 5 (Penkett *et al.*, 1979).

At best, these data establish a lower limit for peroxide oxidation. As discussed above, the $\delta^{18}O$ of atmospheric peroxides may be somewhat lower than that which is finally measured from the ground-based rain collector. It follows that the calculated $\delta^{18}O_{SO_4^{2-}}$ would be correspondingly lower, and the % of sulfate formed by peroxide oxidation would be correspondingly higher.

The technological significance of our findings (that ~40% or more of acid sulfate in rainwater originates from peroxide oxidation of SO_2) is that further investigations of the origin(s) and of possible methods of control of atmospheric peroxides are of prime importance.

SECTION 5

SUMMARY

A new method was developed for the determination of the $\delta^{18}O$ of peroxide (ppb range) in rainwater. Experimental results showed the method to be reliable with respect to recovery of added H_2O_2, blanks, and freedom from isotopic interference. A procedure for collection and treatment of 25-L samples of rainwater with minimum peroxide decomposition between collection and analysis was developed. An isotopic relationship was established between the oxygen in sulfate and the oxygen in the peroxide and in the water involved in the peroxide oxidation of SO_2 to SO_4^{2-}. By using this relationship for peroxide oxidation and a similar relationship previously determined for aqueous metal-catalyzed oxidation, the fraction of sulfates formed by peroxide oxidation in rainwater from four sampling sites in Illinois, North Carolina, New York, and Michigan was estimated to be ~40%. This fraction could be substantially higher if a substantial amount of peroxide undergoes decomposition between the time of oxidation of SO_2 in the atmosphere and the time of collection and peroxide-stabilization treatment of the rainwater sample on the ground. Our results show that atmospheric peroxides play a major role in the formation of sulfates in the atmosphere, and, therefore, that it is essential to obtain all possible information on their origin and control.

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